OXYGEN ISOTOPE PALAEOTEMPERATURE MEASUREMENTS ON AUSTRALIAN FOSSILS

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Abstract

By means of oxygen isotype assays of Cretaceous belemnites and Tertiary mollusca, palaeotemperature determinations have been made of those periods in Australia. Experience gained in this work indicates how a satisfactory general palaeotemperature picture can be obtained by using fossils from shelf faunas. The results also contribute to the fixing of the Pliocene-Pleistocene boundary. The temperatures determined by this physical method agree well with the evidence from biological data.

Introduction

The determination of temperatures of the past by assay of the relative amounts of 0^{18} and 0^{16} in organic carbonates was devised by Urey (1947, 1948), and developed by him and other workers (Urey et al. 1951, Epstein et al. 1951, 1953). Rankama (1954) summarized information on oxygen isotopes available to that date. Emiliani has applied this method to the study of Cainozoic ocean temperatures in the Atlantic and Pacific Oceans, and in the Caribbean and Mediterranean Seas, by the oxygen isotope analysis of deep sea cores (Emiliani 1954*a,b*, 1955*a,b,c*, 1956*a*, 1957, and with Edwards 1953). Calibration of Quaternary palaeotemperature curves by radiocarbon age determinations has thrown new light on the Pleistocene and Holocene, including the problem of human evolution (Emiliani 1956*b*, 1957). Some of the implications of the Pleistocene temperature curve for eustatic changes of sea level have been noted (Gill 1957*a*).

In the present study, a series of Australian Mesozoic and Cainozoic fossils was analyzed. These had necessarily to be from shelf type deposits, and so from sites with a greater variation in temperature than found in the deep ocean habitats. Although this research has been largely exploratory, discovering by experience the materials that are suitable and those not, the results make a positive contribution to our knowledge of the times and area concerned. Detail of the assays is provided in the hope that when more is known about this method, it will be possible to interpret the results more adequately.

All the specimens used for isotope assay are the shells of molluscs, except for some Cretaceous belemnites. Translucent shell was found best for the present purpose.

Controls

Two types of control have been used:

A. Samples from laboratories and sites in the United States of America connected with earlier palaeotemperature measurements. Our standard was the powder of a pale brown translucent rostrum of the belemnite *Peratobelus australis* from the Lake Eyre region, Central Australia. This was compared directly by us with Emiliani's standard PDB II, for which we thank him. Wickman's standard and three small belemnites from the Navesink Formation, Cream Ridge, U.S.A., were also determined. The latter were kindly supplied by Mrs. E. H. Nadeau. The formula used to calculate the temperature was that of Epstein et al. (1953), viz.

$$t\ (^\circ C.) = 16{\cdot}5 - 4{\cdot}3\delta + 0{\cdot}14\delta^2$$

where δ was the per-mil difference in the ratios of masses 46 and 44 of the sample and our standard, which was found to be equal to Urey's standard PDB 1 to ± 0·5°C.

The agreement with Wickman's standard as determined by Emiliani is to ~ 0·2 per-mil for δ, whilst the Cream Ridge belemnites are ~ 1°C. lower than the Lowenstam and Epstein (1954) values for four other specimens from the same formation. As the reproducibility was about 0·5°C. in our results for the same samples, our carbonate temperatures should thus be accurate to within 1°C.

B. Shells of living mollusca from local marine waters, from Macquarie I. in the sub-Antarctic, and from tropical waters to the north.

SITE 1. Hobson's Bay, at Melbourne, Victoria.

This suite of shells was chosen early in the investigation to provide a direct comparison with the fossil shells in the Yarra Delta alongside. When wider studies were undertaken later it was realized that these shells do not provide the best local control in that they belong to an estuarine facies, and salinity affects the isotopic constitution [cf. Epstein et al. (1951), Epstein and Lowenstam (1953), Emiliani (1955*a*)]. Mr. V. G. Anderson has kindly informed us that from chemical tests of water taken at various depths from the lower reaches of the Yarra and Maribyrnong R., the water taken from near the bottom usually consists of undiluted sea-water, while that taken from just below the surface under low-flow conditions may contain from 40 to 80% of sea-water, by volume. There would be greater dilution under flood conditions. Estuarine molluscs have a wide tolerance of salinity conditions (euryhaline). The Fisheries and Game Department of Victoria kindly provided us with salinites measured as concentrations of the chloride ion in parts per thousand of water taken at the surface and at a depth of five metres in Hobson's Bay monthly over a period of five years, and with temperatures taken at the same time at a depth of five metres. In Fig. 2B the temperatures for three years are plotted, showing an annual variation of 9° to 10°C.; the annual mean is 14·4°C.

Assuming that the shells are in equilibrium with the sea-water, a correction should be made for varying O^{18}/O^{16} in that medium. However, in the absence of water samples, or where seasonal variation is to be expected (as in the majority of sites involved here), an approximate correction only can be attempted by considering the normal salinity of the water. Taking the average ocean salinity to be 34·8 per mil, as assumed in the equation of Epstein et al. (1953), a change in salinity of + 0·6 per mil corresponds with a change of about − 1°C., in rough agreement with Epstein and Mayeda's Fig. 3 (1953).

From the Hobson's Bay salinities, a maximum mean value of 35·2 per mil can be estimated, which means that the shells from site 1 can hardly be more than 1°C. too low. Whilst this correction is difficult to estimate, and there is variation for the different years given of ± 1°C. in the Hobson's Bay temperatures measured at 5 metres, the suspicion is that the isotope temperatures are 1° to 2° too low for site 1 (see Figs. 1, 3).

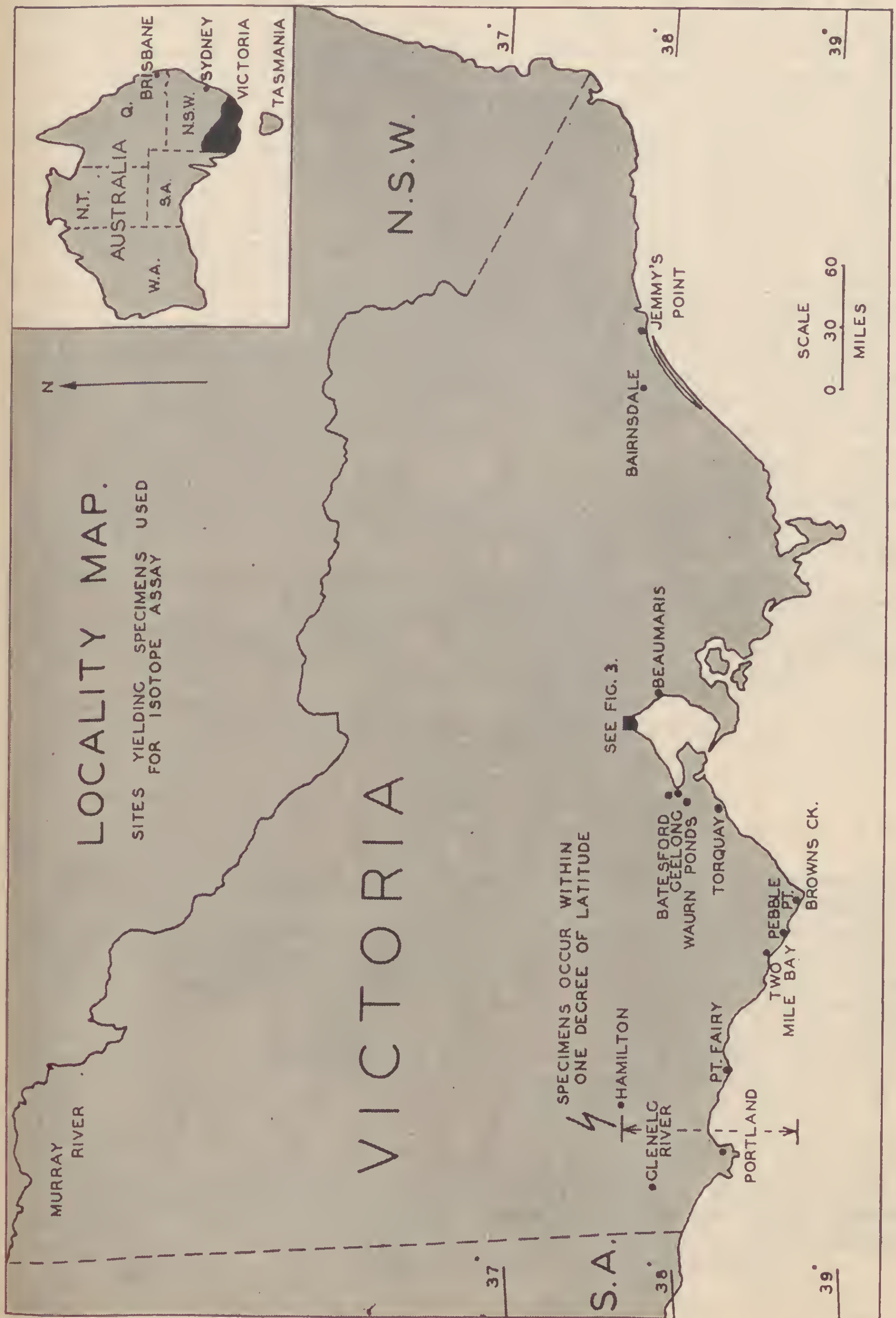
LOCALITY MAP.
SITES YIELDING SPECIMENS USED FOR ISOTOPE ASSAY
N
AUSTRALIA
W.A.
N.T.
S.A.
Q.
N.S.W.
BRISBANE
SYDNEY
VICTORIA
TASMANIA
VICTORIA
N.S.W.
S.A.
MURRAY RIVER
SPECIMENS OCCUR WITHIN ONE DEGREE OF LATITUDE
HAMILTON
GLENELG RIVER
PORTLAND
PT. FAIRY
TWO MILE BAY
PEBBLE PT.
BROWNS CK.
TORQUAY
WAURN PONDS
GEELONG
BATESFORD
SEE FIG. 3.
BEAUMARIS
BAIRNSDALE
JEMMY'S POINT
SCALE
0 30 60
MILES
37°
38°
39°
37°
38°
39°

FIG. 1.

For Macquarie I., the nearby ocean salinities from the *Discovery* Reports (1932-1938) vary between 33·8 and 34·4 per mil for about 55°S. latitude and 145 to 168°E. longitude. As the shells examined were shoreline molluscs, the salinity correction is essentially unknown. The agreement, however, considering the possible variations in measured temperatures and isotope temperatures, is good (see Fig. 2C).

For the Moreton Bay (sub-tropical Queensland) *Anadara* shells, the isotope temperatures may be compared with actual measurements given by Hedley (1915) and the Oceanographical Station Lists, volumes 5 and 15 (kindly supplied by Mr. J. M. Thomson, C.S.I.R.O. Division of Fisheries and Oceanography). The latter give the same mean temperature as Hedley, and also Cl^- as about 19 per mil (34.2 per mil salinity), so that our isotope temperature could be taken to be 1°C. too high. As the disagreement with the direct measurement is then 5 to 6°C., the suggestion is made that the exposure of the animal to atmospheric oxygen at low tide (and possibly also a higher salinity) is responsible. Much remains to be learned on this subject, but it is noted that certain barnacles utilize atmospheric oxygen in the intertidal period (Barnes and Barnes 1957). Another possible variant of the isotopic temperature is the growth habit of the shells. Epstein and Lowenstam (1953) showed a difference of 2°C. in living pelecypods and gasteropods from the shoal waters of Bermuda.

No correction has been made for varying C^{12}/C^{13}, as variation here should not introduce any appreciable error. Such corrections have not been made by previous workers (Urey, Epstein, Emiliani, et al.) although a paper by Craig (1957) claims that errors up to $\sim$ 3°C. are possible.

Another factor that may be worth consideration is the mixing of atmospheric oxygen in surficial ocean waters by wave action.

Molluscs from Hobson's Bay, provided by Miss J. Hope Macpherson, yielded the following oxygen isotope temperatures:

Specimen 1.	*Callanaitis disjecta* (Perry)	10·4°C.
	Duplicate assay	9·9°
2.	*Eumarcia fumigata* (Sowerby)	11·5°
3.	*Eumarcia fumigata* (Sowerby)	11·5°
4.	*Katelysia rhytiphora* (Lamy)	11·0°
5.	*Paradione kingii* (Gray)	11·0°
6.	*Polinices conicus* (Lamarck)	10·7°
	Average	11·0°

Specimens 1-6 belong to a sandy facies, and come from the sandy part of Hobson's Bay between St. Kilda and Port Melbourne.

Duplicate or triplicate assays refer to a fresh preparation of CO_2 from the same sample powder, and give an estimate of the experimental reproducibility. All duplicates were performed some considerable time after the original assay, the powder being stored over silica gel.

SITE 2. The following tropical mollusca were assayed:

Specimen 7.	*Cypraea (Mauritia) depressa* Gray Funafuti Island	20·6°C.
8.	*Nerita polita* Linnaeus	21·2°

The white lip of the Cypraea was used for the assay.

SITE 3. Shells from a sub-tropical environment were also used in the control series, *Anadara* from Moreton Bay, Queensland, collected by Mr. F. S. Colliver, being assayed.

Specimen 9.	*Anadara* aff. *trapezia* (Deshayes)	15·8°C.

This lamellibranch is an intertidal estuarine form, and lives half buried in mud (see Hedley 1915, Fig. 14). The oxygen isotope temperatures calculated from assays of shells of this genus (both extant and fossil) are consistently low. This suggests that there is a factor associated with the biology of this animal. As *Anadara* spends half its time at a mud-estuarine water interface, and the other half at a mud-air interface, its mode of life may well account for the results obtained. Reference has already been made to the variation in the isotope temperatures of molluscs in the shoal waters of Bermuda (Epstein and Lowenstam 1953). It has been learned from the present series of assays that variation in isotope temperature may occur from species to species and genus to genus. The results from a given genus are internally consistent but are offset by a given factor from assays made on certain other genera. Thus one may speak of *Anadara* temperatures, *Ostrea* temperatures, and so on (cf. Epstein and Lowenstam 1953). Therefore, more consistent results can be expected by selecting a suitable genus and doing all the required assays on specimens from it, using where possible the same species, or at least species from the same facies. Such a procedure will give sounder relative temperatures, but for absolute temperatures the mean of a number of representative species should be taken. As Epstein and Lowenstam (1953) have indicated, "no single species can be used for determining the average palaeotemperatures or the palaeotemperature ranges".

Anadara specimens often appear in the succeeding series of Quaternary fossils used for assay because it is a stenothermal form, locally at the extreme of its range, and so useful in tracing changes in mean temperature. *Anadara trapezia* is so plentiful in intertidal mud flats at Port Jackson that it is commonly known as the Sydney Cockle. In Port Phillip it is rare and found only below low tide, because it is at the southern extreme of its range and is unable to withstand the low winter temperatures on exposed mud flats. Only 5,000 years ago, however, the species was present in millions in Port Phillip, as crowded fossil beds (dated by radiocarbon) clearly indicate (Gill 1955*b,c,* 1956). During the colder periods the species was locally absent, while in warmer periods it migrated as far south as Flinders I., NE. Tasmania. There is a specimen of *Anadara* from Flinders I. in the Dennant Collection in the National Museum of Victoria. It is very worn and may have been collected from the beach. Mr. R. W. T. Wilkins collected a worn *Anadara* from the beach at Opossum Boat Harbour, E. of Lady Barron.

SITE 4. Macquarie I. Shells from the sub-Antarctic provided control specimens from a colder regime.

Specimens 10-12 are all *Nacella delesserti* Philip, a limpet. The three specimens gave tempertures of 2·6°, 3·0°, and 3·7°C. respectively. The first two were encrusted with algae and serpulid calcareous tubes, but these were removed before assay. The algae gave a greenish powder which yielded $0^{18}/0^{16}$ temperatures of 11° and 16°C. These high temperatures are undoubtedly due to the organic matter in the samples. As a shoreline mollusc, *Nacella* would presumably be exposed to the air for a part of each day, and so it is not an ideal shell on which to make temperature measurements. However, it was the only species available at the time. Mr. P. G. Law, Director of the Antarctic Division, kindly supplied sea-water temperatures from Macquarie I. taken daily at 10 a.m. from May 1951 to March 1952, and these gave a mean of 5·3°C. (see Fig. 2C).

The results from the controls are summarized in Table 1.

That these four controls are in the correct order, and related to actual temperatures recorded (see Fig. 2) indicates that the method is dependable, in general at any rate. The results are relatively correct, but in absolute figures are consistently lower.

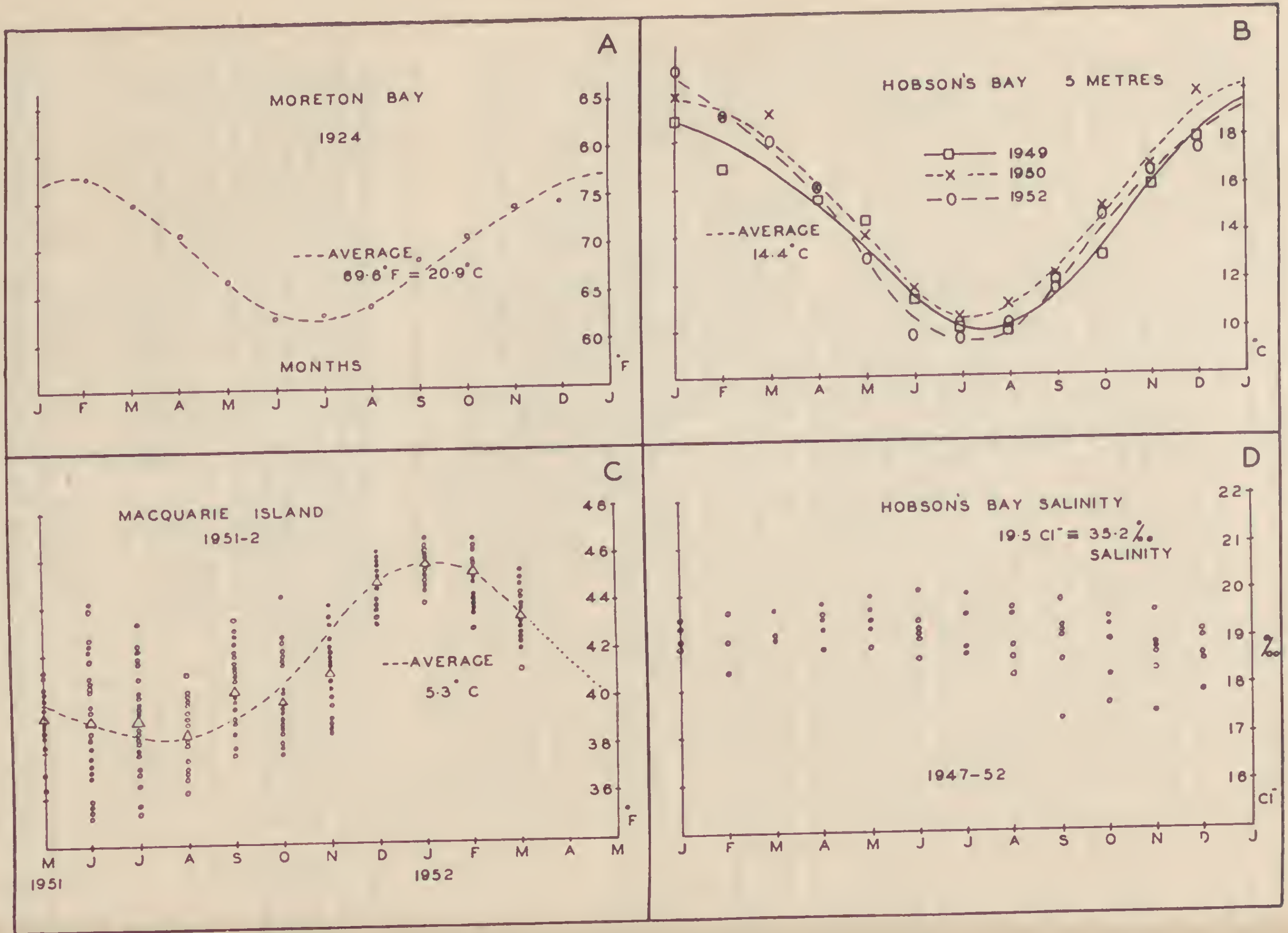

Fig. 2.—Recorded temperatures and Hobson's Bay Salinity.

TABLE 1

Zone	Oxygen isotope temperature °C.	Direct Measurement °C.
Tropical	20·9	———
Sub-tropical (Queensland) ..	15·8	20·9 (Hedley 1915, Rochford and Spencer 1952-3)
Temperate (Victoria)	11·0	14·4 (Fisheries and Game)
Sub-Antarctic (Macquarie I.) ..	3·1	5·3 (Antarctic Division)

These differences can probably be explained by corrections for salinity, absorption of atmospheric oxygen, and growth habits of the molluscs.

Fossils

The first suite of fossils is from a grey clayey silt formation of the Yarra Delta, which extends for some miles up the Maribyrnong and Yarra R. The geological age of mid-Holocene has been confirmed by a radiocarbon dating which was carried out on a piece of wood bored by marine borers found in a shell bed at the top of this formation at a locality about 7 m. from Hobson's Bay on the Maribyrnong R. The date obtained was 4,820± 200 years (Gill 1956).

The facies involved with all these specimens is estuarine, and so the salinity would not be a normal marine one. Mr. A. C. Collins examined some of the matrix from the Appleton Dock site (see Fig. 3) and recognized the following foraminifera: *Streblus* aff. *beccarii* (Linnaeus), *Elphidium incertum* (Williamson), *Elphidium* sp. The presence of these genera to the exclusion of normal marine genera is characteristic of the estuarine facies.

SITE 5. The Yarra Delta (detail in Fig. 3).

Specimen 13. *Anadara trapezia* (Deshayes). West Melbourne Swamp. Lives three-quarters buried in estuarine mud, usually between tidemarks 10·0°C.

14. *Anadara trapezia*. From 17 ft. below the surface at the Gas Works, West Melbourne. Presented by Mr. R. Boyes .. .. .. 9·2°

15. *Anadara trapezia*. From excavation for Appleton Dock, Melbourne. Collected by E. D. Gill 6·8°

16. *Anadara trapezia*. From Newport, suburb of Melbourne . .. . 8·4°

17. *Anadara trapezia*. From between 6 and 12 ft. below the surface at about the centre of Fishermen's Bend, R. Yarra, Melbourne. Presented by Mr. J. F. Hill .. .. 9·9°

18. *Fasciolaria australasia* (Perry). Crawls on rocks below low water. From same locality as specimen 16 .. .. 10·2°

19. *Pecten fumatus* Reeve (formerly called *P. medius*). Lives on sea floor. From West Melbourne Swamp .. .. 9·1°
Duplicate assay .. .. 9·5°

20. *Polinices sordidus* (Swainson). Formerly called *P. plumbeum*. Lives on sea floor. From West Melbourne Swamp; collected by Dr. G. B. Pritchard .. .. 11·9°


MELBOURNE
AND ENVIRONS
SITES YIELDING
SPECIMENS USED FOR
ISOTOPE ASSAYS
N
SCALE
0 MILES 1
OLYMPIC PARK
YARRA RIVER
ST. KILDA
WEST MELB. GAS WORKS
FISHERMENS BEND
YARRA DELTA
PORT MELBOURNE
HOBSON'S BAY
WILLIAMSTOWN
APPLETON DOCK
WEST MELBOURNE SWAMP
COODE CANAL
MARIBYRNONG PARK
MARIBYRNONG RIVER
NEWPORT
MILLER'S ROAD
EMERGED SHELL BEDS
KOROROIT CREEK
LAKE SEAHOLME
ALTONA

Fig. 3.

21. *P. sordidus.* From Olympic Park, Melbourne. One of the fossils mentioned by Pritchard (1910) .. .. 11·0°

22. *P. sordidus.* From left bank Maribyrnong R. Essendon, near Maribyrnong Park. Collected by E. D. Gill .. .. 11·4°

The grey clayey silt in which these fossils were found forms a surficial layer of 20 to 30 ft. in the Yarra Delta, and overlies an oxidized marine formation of similar material on which a terrestrial physiography has been eroded and at the surface of which a fossil soil is sometimes preserved. Channels extending to 100 ft. below present low sea level are known in the oxidized formation, and these channels are infilled with the grey clayey silt, which has little bearing weight and is a problem to engineers. In the lower part of these channels there are few shelly fossils, but estuarine diatoms are found which include forms not found in the higher part of the formation. Only in the top part of the formation is *Anadara* found. The low channels were cut during the last lower level of the sea (Mankato) as shown by radiocarbon dating as well as the general geology (Gill 1955 *a,b,c*. 1956, 1957*a*). The sediments in the bottom of the channel were therefore probably laid down during times colder than the present, while the top part of the formation was laid down in times slightly warmer than the present, judging by the abundance of the stenothermal lamellibranch *Anadara*. The lower the level from which shells in this formation come, therefore, the lower probably was the mean temperature. This may account for some of the differences of temperature observed in the present series. E.g. taking the *Anadara* temperatures, the variation relative to depth is as follows:

Surface (Specimen 13)	10·0°C.
6-12 ft. (Specimen 17)	9·9°
17 ft. (Specimen 14)	9·2°
Excavation of unrecorded depth (Specimen 16)	8·4°
Near bottom of formation (Specimen 15)	6·8°

Specimen 16 is fitted into this series according to where its oxygen temperature indicates, but it is significant that the other four temperatures are related to the depth at which the specimens occurred in the formation (see Fig. 4), although it should be observed that the difference between specimens 13 and 17 is not significant.

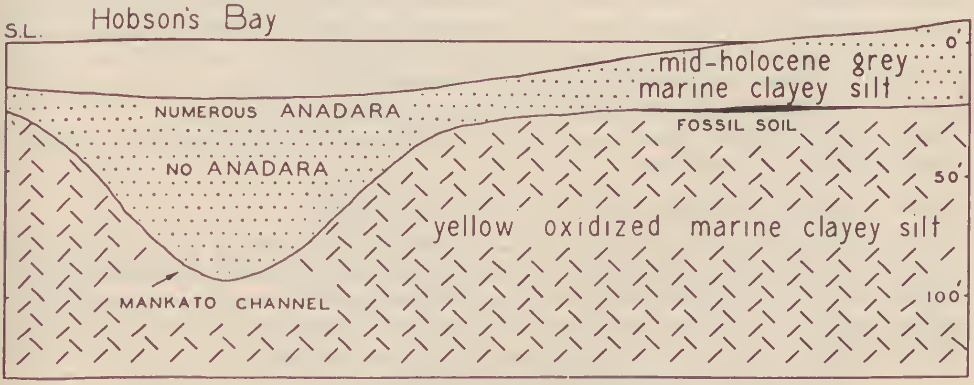

FIG. 4.—Diagrammatic geological cross-section of Hobson's Bay.

The three specimens (nos. 20-22) of *Polinices* come from widely dispersed sites but all from the top of the formation, so that the temperatures are relatively high.

As a future experiment it would be interesting to take a series of specimens of the same species from various levels at the same site in the grey clayey silt of the Yarra Delta in an effort to trace the rise in temperature that accompanied the Flandrian transgression.

Upper Pleistocene Fossils

SITE 6. Port Fairy. The ecology of this site contrasts with that of the estuarine facies of the Holocene fossils just discussed. The Port Fairy shell bed is a beach deposit of the open coast, protected only by reefs of basalt which extend out into the sea. The site has been described, and its age shown to be beyond the range of radiocarbon (Collins 1953, Gill 1953, 1955*c*, 1956). It is thought to be Sangamon in age. The shells of the old beach are mostly broken, and mixed with basalt boulders and sand. Some of them are rock shells and some sand shells. This fossil beach is approximately 25 ft. above the present one.

Specimen 23.	*Cellana tramoserica* (Sowerby)	8·2°C.
24.	*Floraconus anemone* (Lamarck)	10·8°
25.	*Mactra australis* Lamarck	9·5°
26.	*Mactra pura* Deshayes	11·4°
27.	*M. pura* Deshayes	9·4°
28.	*M. pura* Deshayes	9·5°
29*a*.	*Ninella torquata* (Gmelin)	8·6°
29*b*.	*N. torquata* (Gmelin). Different part of same shell as 29*a*.	9·3°
30.	*Scutus antipodes* Montfort	9·5°

Mactra is a sand shell, while *Cellana, Ninella,* and *Scutus* are rock shells, generally intertidal. *Floraconus* lives in rock pools under rocks or partly buried in sand near low water or below. It is a lower littoral mollusc that frequents the open coast or bays where there is some shelter, but it is not estuarine.

The biological evidence suggests warmer waters than the present because of the occurrence of sub-tropical genera of foraminifera (Collins 1953), and the gasteropod *Ninella torquata* which is now extinct on this coast but lives further north. The physical evidence from oxygen isotope assay of foraminifera from deep sea bore cores (Emiliani 1955*a*, Suess 1956) suggests that the Sangamon temperatures were similar to those of postglacial time. The biological evidence in Australia agrees with this, as also do the present analyses in that the average for the mid-Holocene beds is 9·8°C. and those for Port Fairy 9·6°C. The results are fairly consistent, except that specimens 26 and 27, although of the same species, vary by 2°C.

It is suspected that either contamination has occurred, or the analyses are more variable than they should be.

SITE 7. Emerged shell beds, Altona, Victoria (see Fig. 3).

This deposit has been described by Hills (1940), but its dating is still uncertain. In fact, it appears likely from recent researches that two ages may be involved, viz. Pleistocene beds over which are mid-Holocene beds such as seen in the excavations for the bridge in Miller's Road over the creek that drains Lake Seaholme. Both deposits contain *Anadara*. The fossils analyzed are as follows:

Specimen 31.	*Flavomala biradiata* (Wood)	4·2°C.
32.	*Katelysia rhytiphora* (Lamy)	8·0°

33.	A second shell of the above species	8·2°
34.	*Polinices conicus* (Lamarck)	6·8°
35.	*Pseudarcopagia victoriae* (Gatliff and Gabriel)	7·8°

All these molluscs belong to a sand facies. The *Flavomala* temperature appears to be erroneous, and the *Polinices* temperature is low. These could only be correct if they represent the advance of the sea from the previous glacial low sea level. The above results, and the observations made in the interim by one of us (E.D.G.) indicate that a more critical study of the stratigraphy of the Altona shell beds is required.

SITE 8. Two Mile Bay, W. of Port Campbell, Victoria (Baker and Gill 1958).

This site consists of an emerged marine platform 10 to 11 ft. above the present one, both being cut in consolidated Miocene marine yellow earthy limestone. On the fossil platform are beach sands with marine shells, all now covered by lagoonal and dune deposits, as well as talus materials from the former marine cliffs behind the platform. A radiocarbon analysis was made for a specimen of *Ninella torquata*, which is a warmer water shell not now living on this coast, but it was beyond the range of this dating method. Because of the radiocarbon date and evidence of a lower sea level since the platform was cut, the feature is thought to be of Sangamon age. The fossils of which oxygen isotope analyses were made are:

Specimen 36.	*Cellana tramoserica* (Sowerby)	10·4°C.
37.	*Dicathais textiliosa* (Lamarck)	7·7°
38.	*Ninella torquata* (Gmelin)	8·6°

These are all gasteropods which live on a rocky substrate, between or near tide-levels. There is no obvious reason for the disparity between these results.

Lower Pleistocene Fossils

The Werrikooian Stage (Singleton 1941) has been placed by some in the Upper Pliocene and by others in the Lower Pleistocene. Now that the Plio-Pleistocene boundary has been fixed by international convention, it is possible to determine where the Werrikooian Stage should be placed. It is considered to belong to the Lower Pleistocene (Gill 1957*b*).

SITE 9. "Singleton's Outcrop", on the right bank of the Glenelg R. near Myaring Bridge, N. of Nelson, Victoria (Singleton 1941).

Specimen 39.	*Dosinia* sp. (large)	12·3°C.
	Duplicate assay	12·2°
40.	*Dosinia* sp. smaller shell than specimen 39	8·7°
41.	*Glycymeris pseudaustralis* Singleton	8·2°
42.	*Glycymeris* sp.	9·2°
43.	*Glycymeris* sp. Different shell from specimen 42	8·5°
44.	*Glycymeris* sp.	5·5°
	Duplicate assay	5·2°
45.	*Glycymeris* sp.	6·9°
	Duplicate assay	7·8°
46.	*Katelysia* sp.	8·2°
47.	*Limopsis werrikooensis* Singleton	8·2°
48.	Ditto. Different shell from specimen 47	8·2°
49.	*Ostrea sinuata* Lamarck	11·4°

50. *Placamen subroborata* (Tate) .. .. .. 11·1°
51. *Scacolcda crassa* (Hinds) .. .. 5·3°
52. Ditto, different specimen .. .. 5·9°

These specimens belong to a sandy or muddy sand environment, and were collected by E.D.G. The palaeotemperature results for some of these specimens (e.g. 44-45, 51-52) appear to be too low; a check assay of specimen 44 confirmed the earlier measurements, while that on specimen 45 gave a higher temperature. The reasons for the variations are not understood. It would appear that either there has been ionic exchange and/or the shells represent different levels in the deposit having different temperatures, and/or the species have different growth habits. The first possibility is real in that many of the shells at this locality were chalky and somewhat altered. Nevertheless, those selected for assay appeared to be well preserved. The shells used have been kept, so that later checks can be made if deemed desirable. As they stand, the palaeotemperatures obtained give an average of 8·4°C.

In review of the Quaternary isotope palaeotemperatures, it may be concluded that without corrections the isotope assays cannot follow the small changes of Quaternary mean temperature when based on littoral mollusca. The seasonal changes are so great as to mask the small changes in mean temperature effected by changes in Quaternary climate, and the growth habits of the molluscs concerned are unknown.

Upper Pliocene Fossils

SITE 10. The Maretimo Member of the Whaler's Bluff Formation consists of beds similar lithologically to the Werrikoo Member and immediately underlying them without any discernible sedimentational break. The name was included by Boutakoff and Sprigg (1953) in a stratigraphical table, but no definition has yet been published. However, the authors have indicated (personal communication) that the section on which it is based is in Dutton Way on the N. side of Portland, Victoria. The Werrikoo Member (as defined by Singleton 1941), when traced to the coast, is found to have beneath it similar and conformable beds which have now been called the Maretimo Member. The following fossils collected by E.D.G. were used for O^{18}/O^{16} analysis:

Specimen 53. *Ostrea sinuata* Lamarck (mud oyster) .. 13·9°C.
Duplicate assay (translucent flakes of shell were used) .. .. 13·6°
54. *Ostrea sinuata* Lamarck .. .. 13·0°
55. Another shell of the same species .. .. 13·1°
56. Another shell of the same species .. .. 13·0°
57. *Aloidis* (*Notocorbula*) cf. *coxi* (Pilsbry) .. 11·8°
58. Another shell of the same species .. .. 11·8°

These shells are of muddy sand to sand facies. Epstein and Lowenstam (1953) found that at Bermuda some species grew their shell "during the large fraction of the temperature range", while other species retain shell growth mostly for a given temperature range. Such effects could be present in specimens 54 to 58 where there is a consistent difference in the assays from the two species of lamellibranchs. The mean value for the assays of Maretimo shells is 12·8°C.

Although the Maretimo and Werrikoo Members are similar in facies and preservation, and are stratigraphically conformable, there is a definite temperature difference. The highest temperatures of the Maretimo series are higher than those of the Werrikoo, the average is higher (even omitting the temperatures in the Werrikoo series that appear to be too low), and what is probably the most significant, temperatures for shells of the same species are higher, viz. *Ostrea sinuata* gives an isotope temperature of 11·4°C. for the Werrikoo and 13·2°C. (average of five assays of four specimens) for the Maretimo. This is of particular interest because on biological evidence the base of the Werrikoo was selected as the base of Pleistocene (Gill 1957*b*), i.e. the approximate time at which the lowering of mean temperature at the end of the Tertiary reached a point comparable with the present before descending into the cold of the initial Pleistocene glaciation. The physical evidence from the oxygen isotope palaeotemperatures thus fits the biological evidence.

Lower Pliocene Fossils

A considerable period of time separates the Maretimo and Kalimnan. No stages have yet been established for this time, and no beds of this age are known in Victoria. The reason may be that this was the time of major uplift during the Kosciusko movements (David ed. Browne 1950). However, marine beds on Flinders I. in Bass Strait may represent part of this period between Maretimo and Kalimnan.

In the present series, molluscs from the type Kalimnan beds at Lakes Entrance (see Singleton 1941), and from the well-known beds near Hamilton, were assayed for their palaeotemperatures, as follows:

Site 11. Jemmy's Point, Lakes Entrance, Gippsland, Victoria.

Specimen 59.	*Bassina paucirugata* (Tate)	10·8°C.
60.	*Eucrassatella kingicoloides* (Pritchard)	9·5°
61.	Another specimen of same	7·9°
62.	Third specimen of same	7·1°
	Duplicate assay	6·9°
	Another part of same shell	7·1°
63.	*Placamen subroborata* (Tate)	10·4°

Site 12. Upper bed, Forsyth's Bank, Grange Burn, near Hamilton, W. Victoria (locality 6, Gill 1957*c*, page 144).

Specimen 64.	*Cleidothaerus* cf. *albidus* (Lamarck)	8·7°C.
65.	*Ostrea manubriata* (Tate) Shell discloured but hard	13·2°

Site 13. Upper bed, Muddy Creek, near Hamilton, Victoria (locality 1, Gill 1957*c*, page 144).

Specimen 66.	*Bassina paucirugata* (Tate)	11·4°C.
67.	*Glycymeris* (*Tucetona*) *convexa* (Tate)	10·7°
68.	*Glycymeris halli* Pritchard	10·7°
69.	*Sunemeroe gibberula* (Tate)	11·4°

There is a great deal of variation in the results from Lakes Entrance. The beds there are more exposed to leaching agencies than at Hamilton where the beds are protected by a shield of basalt. The evidence from the foraminifera (Parr 1939), and the wealth of the gasteropod *Tylospira* and the echinoderm *Arachnoides* indicate waters a little warmer than the present. The *Ostrea* temperature is consistent with the others obtained so far, and the two *Glycymeris* temperatures are clearly higher than those of the Werrikooian, even when some allowance is made for possible ionic contamination. The *Eucrassatella* temperatures are variable and low, yet internally consistent when checked, viz. the three determinations on specimen 62.

Upper Miocene Fossils

SITE 14. Fossiliferous marine strata exposed in sea cliff at Beaumaris, Victoria, viz. the type locality of the Cheltenhamian Stage (Singleton 1941, Gill 1957*c*). The upper beds have been "lateritized" and this makes it difficult to obtain shells suitable for isotope assay even from the least affected stratum at the base of the cliff. Beneath 8 ft. of more recent windblown sands, there are 19 ft. of ferruginous sandstones, then 17 ft. of mottled to fawn marly sand to sandy marl, under which again are 3 ft. of brown sandstone with numerous shells (many powdery) in the vicinity of highwater level.

Specimen 70.	*Glycymeris halli intermedia* Pritchard	14·2°C.
	Duplicate assay	13·2°
71.	*Monia* cf. *ione* (Gray)	11·7°
72.	Another specimen of same species	11·2°
73.	*Ostrea* sp.	14·3°

The thinness of the shell in *Monia* may be a factor in the lower temperature obtained for specimens 71 and 72. The results from the other genera are consistent.

The biological evidence for the warmer temperature of the sea of this time is provided by the numerous sharks and rays, the numerous echinoderms *Lovenia, Arachnoides* and *Clypeaster,* molluscs such as *Cucullaea* and *Tylospira*, and foraminifera such as *Amphistegina* and *Orbulina.*

SITE 15. Marine strata exposed in left (E.) bank of the Tambo R. just S. of the Princes Highway bridge at Swan Reach, Gippsland, Victoria. The age of site 15 has been given at Mitchellian (Crespin 1943) which may be equivalent to Cheltenhamian, or partly so.

Specimen 74.	*Chlamys antiaustralis* (Tate)	16·7°C.
75.	Another shell of the same species	16·7°

The assays are internally consistent, but higher than those for shells of the same or similar age. It is noted that the palaeotemperatures for *Chlamys* in the Balcombian sequence are likewise the highest. The explanation may well be biological.

Middle Miocene Fossils

SITE 16. Limestone formation at Bairnsdale, Gippsland, Victoria.

This formation is the type of the Bairnsdale Substage (Balcombian Stage) of Crespin (1943*b*), which the writers prefer to regard as a stage, retaining the term Balcombian for the beds at Balcombe Bay as originally defined by Hall and Pritchard (1902), then more rigidly defined by Singleton (1941). The following specimens were taken from the Sweet Collection in the National Museum of Victoria:

Specimen 76.	*Hinnites corioensis* McCoy	11·2°C.
	Duplicate assay	11·2°
77.	*Ostrea* sp.	10·8°
	Other assays of the same shell gave	9·2° and 9·4°
78.	*Ostrea* sp. Different shell	16·5°
79.	*Spondylus pseudoradulus* McCoy	16·6°

The facies is a limestone one, i.e. mostly organic carbonate and with but a small percentage of terrigenous sediment. There has been transport of minerals so that no aragonitic fossils remain, and there is a good deal of cementation by secondary calcium carbonate. The shells used are all calcitic ones, as preserved.

SITE 17. Beach of Corio Bay at North Shore, Geelong, Victoria.

Dr. O. P. Singleton has kindly advised that in his opinion this site is also Bairnsdalian in age. The following calcitic shells were assayed:

Specimen 80.	*Hinnites corioensis* McCoy	15·7°C.
81.	*Serripecten yahlensis* (McCoy)	13·9°

Lower Miocene Fossils

SITE 18. Balcombe Bay near Mornington, Port Phillip, Victoria. This is the type area for the Balcombian Stage (Singleton 1941 and references).

Specimen 82.	*Spondylus pseudoradulus* McCoy	13·8°C.
83.	*Chlamys* sp.	16·8°
	Duplicate assay	16·8°

The matrix at Balcombe Bay is a calcareous siltstone. The aragonitic shells, although morphologically perfect, show a degree of alteration, but the calcitic shells appear to be unchanged. The palaeotemperature for specimen 82 is probably too low, both by reason of the results from assays of other specimens (e.g. a shell of the same species from the Middle Miocene of Bairnsdale gave a temperature of 16·6°C.), and by reason of the biological evidence. The latter indicates a tropical climate in Victoria during the period concerned, viz. numerous and large tropical foraminifera such as *Lepidocyclina* (Crespin 1943*a*); echinoderms such as *Brochopleurus, Phyllacanthus, Eucidaris* (Fell 1954), *Clypeaster,* and *Lovenia;* the mullusca include some two dozen species of cowries (including giant forms), some three dozen species of ornate gasteropods of the *Murex* type, many of the *Columbella* type, and other tropical genera such as *Argobuccinum.*

SITE 19. The lower marine formation along Muddy Creek, and in places on Grange Burn, near Hamilton, Victoria (for map see Gill 1957*c*). The "lower beds", as they are called in the literature (= Muddy Creek Marl), underlie a formation of Kalimnan age (= Grange Burn Coquina), while in between is a layer of phosphatic nodules with evidence of a disconformity. The lower beds are referred to the Balcombian Stage (Singleton 1941).

Specimen 84.	*Chlamys murrayanus* (Tate)	20·1°C.
85.	*Glycymeris cainozoica* (Woods)	16·8°

The former shell is partly calcitic and partly aragonitic, while the latter is aragonitic. While there is 3·3°C. difference between these two assays, the generally higher temperatures for the mid-Tertiary are maintained.

SITE 20. Cement company's quarry at Batesford, about 4 m. NW. of Geelong, Victoria. This is the type locality for the Batesfordian Stage (see Singleton 1941). There has been some discussion as to whether or not this Stage is but a facies variant of the Balcombian. However, siltstone with a fauna referred to the Balcombian overlies the Batesford Limestone, so that if there is any contemporaneity, the Batesfordian is equivalent to but part of the Balcombian. The following specimens from the Batesford Limestone were assayed:

Specimen 86.	*Chlamys murrayanus* (Tate)	21·1°C.
87.	*Linthia* sp.	21·3°
	Triplicate assays	20·8° and 20·6°
88.	*Phyllacanthus duncani* Chapman and Cudmore	13·5°
	Duplicate assays	14·0°

All these specimens are calcitic. The cidarid remains (*Phyllacanthus*) were included in the series because they are a warm water indicator, but since they were selected, Rasmussen (1956) has pointed out that echinoids are unsuitable for oxygen isotope palaeotemperture measurements (see also Urey 1948*b*). The results for specimen 88 may therefore be left out of consideration for the present. The high isotope temperature is in keeping with the masses of *Lepidocyclina* and other tropical foraminifera found in the Batesford Limestone (Crespin 1943*a*).

Oligocene Fossils

SITE 21. Formation exposed in the sea cliffs at and in the vicinity of Bird Rock, near Torquay, Victoria. This is the type locality for the Janjukian Stage (see Singleton 1941 and references, Raggatt and Crespin 1955). All the specimens assayed from this site are from the Jan Juc Formation of Raggatt and Crespin.

Specimen 89.	*Chlamys* sp. (½ in. diameter)	16·8°C.
90.	*Chlamys* sp. (1½ in. diameter)	16·8°
91.	*Cucullaea corioensis* McCoy	16·5°
	Duplicate assay	16·0°
92.	*Eotrigonia* cf. *intersitans*	13·3°
93.	*Glycymeris ornithopetra* Chapman and Singleton	14·2°
	Duplicate assay	13·9°
94.	*Graphularia robinae* McCoy. Hard white interior used	23·9°
95.	*Spondylus gaderopoides* McCoy	16·3°
96.	Another specimen of same species. Hard white outer layer used	17·5°

Of the above skeletons, the following are aragonitic—*Chlamys* (in part), *Cucullaea, Eotrigonia,* and *Glycymeris,* while the following are calcitic—*Chlamys* (in part), *Graphularia,* and *Spondylus.*

The *Graphularia* from both sites 21 and 22 yielded isotope temperatures higher than the other animals. The reason could well be biological, as the animal is an octocorallian coelenterate and lives partly buried in the sediments of the sea floor. The aragonitic molluscs *Glycymeris* and *Eotrigonia* appear to be on the low side, but the rest are uniform.

SITE 22. Lime quarries on the S. side of the Princes Highway at Waurn Ponds, W. of Geelong, Victoria (see Quarter Sheet 28 NE., Geological Survey of Victoria, and Coulson 1930).

Specimen 97.	*Chlamys* sp.	22·8°C.
98.	*Graphularia robinae* McCoy	23·6°
99.	*Ostrea* sp.	17·5°
	Duplicate assay	18·4°

The fauna of site 22 is considered to be Janjukian, i.e. of the same age as the Jan Juc Formation at Torquay.

Eocene Fossils

SITE 23. Brown's Creek, Cape Otway district (see Singleton 1941).

Specimen 100.	Cidaroid spine	13·4°C.
101.	*Notostrea tarda* (Hutton)	12·7°
	Duplicate assay	13·2°

Both the above specimens are calcitic.

SITE 24. Hamilton Creek, Cape Otway district (see Singleton 1941).

Specimen 102. *Notostrea tarda* (Hutton) .. .. 13·8°C.

103. cf. *Serripecten yahlensis* (McCoy) .. .. 13·0°

The palaeotemperatures are consistently lower than for the Middle Tertiary, and they are internally consistent.

Paleocene Fossils

SITE 25. Beds at Pebble Point, Otway Coast, Victoria. This is the same formation as represented by Wilkinson's No. 6 locality. For maps and discussion see Singleton (1941), and Baker (1943). Although the fossils concerned have been described as Eocene, they are now widely thought to be of Paleocene age. They are older than those from sites 23 and 24.

Specimen 104. *Lahillia australica* Singleton .. .. .. 10·6°C.

105. Another specimen of the same species from a different collection .. .. 11·8°

Material suitable for assay is not readily obtainable from this site, but further palaeotemperature determinations are desirable before a conclusion is reached. However, on the present evidence the mean temperature in the Paleocene in the Otway area was less than in the Eocene and represents a further decline from the mid-Tertiary tropical climate.

Review of Tertiary Palaeotemperatures

In spite of the many difficulties encountered in this investigation, the general results present a clear picture of higher temperatures in the mid-Cainozoic, but falling away from this peak in both the earlier and later Cainozoic. This is shown by the graphs in Fig. 5. The lines representing the palaeotemperatures yielded by the

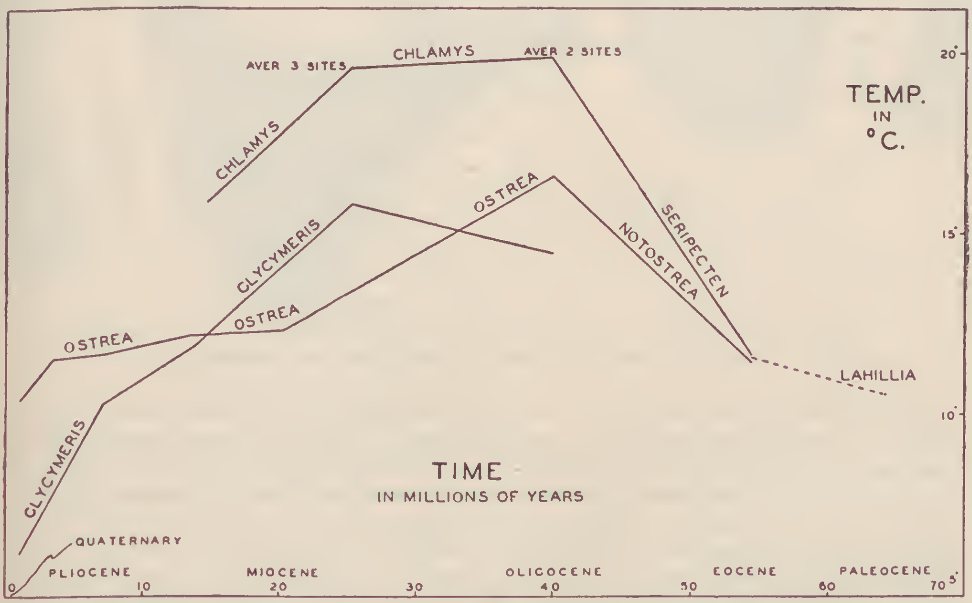

FIG. 5.—Tertiary oxygen isotope temperatures.

oysters (*Ostrea* and *Notostrea*), scallops (*Chlamys*) and *Glycymeris* present the same picture, but no series is complete. The experience gained by this group of assays indicates that where possible the one genus (a calcitic one for preference) should be followed right through the stratigraphical succession as far as possible.

When this work was first initiated, a series of "*Natica*" shells from every geological period from the Eocene to the present was selected, but it was found that although the shells were morphologically complete, many had been altered by ionic exchange.

Cretaceous Fossils

During the Cretaceous Period, the Australian region was trisected by a central sea as shown in Fig. 6.

Fig. 6.—Cretaceous palaeogeography. (After David ed. Browne 1950.)

All the specimens assayed came from this central sea, and not from the geosynclinal areas that bordered the Australian region. The specimens from the Lake Eyre district are belemnites (Glaessner 1957), and were used not only to determine the general level of temperature, but also to show the variations in temperature during the life of the animal as exhibited by the changing O^{18}/O^{16} ratios in the successive layers of the skeleton. The results of the latter project are summarized in Fig. 7 where the isotope temperatures of the successive sections (as marked by dark rings— see Pl. VIII) are plotted. In Fig. 7C, e.g. the earlier stage of growth represents a maximum temperature, and there are succeeding lower temperatures till half-way through the shell, where they rise again to the maximum at the external surface of the shell. The following specimens were assayed:

A. Central Australia—Lake Eyre district, approximately 28°S.

Specimen 106.	*Peratobelus oxys* (Tenison-Woods), Primrose Springs. Middle Lower Cretaceous (Aptian)	13·8°C.
107.	*Dimitobelus diptychus* (McCoy), "Wood Duck Creek and Peake Station"	15·0°
108.	*Peratobelus australis* (Phillips), "Lake Eyre". Middle Lower Cretaceous (Aptian)	16·5°
109.	Belemnite from Lake Eyre, 10 mm. diameter	13·7°
110.	Ditto 8 mm.	12·2°
111.	Ditto 9 mm.	13·7°

A cross-section of specimen 108 was our standard sample. Duplicate assays gave —0·31 per mil and —0·22 per mil relative to Emiliani PDB II = 0·28 ± 0·10 per mil on Urey's scale of PDB I = 16·5°C. (Epstein et al. 1953). The mean value of δ was taken as —0·27 ≡ 0·28 ± 0·10 per mil (PDB II). Our standard relative to Wickman's standard gave —15·3 and —15·6 per mil. Emiliani got —15·38 ± 0·10 per mil for Wickman's standard relative to his on Urey's scale.

B. Queensland—Roma district, approximately latitude 26°S.

Specimen 112.	*Maccoyella* sp. 5 m. SE. of Roma. Middle Lower Cretaceous (Aptian)	21·1°C.

These palaeotemperature determinations are for a different area from that which yielded the Tertiary specimens. Direct comparisons are therefore not possible.

C. U.S.A.—Shank Farm, Cream Ridge, New Jersey. Three small belemnites collected by Dr. H. Richards and Mrs. E .H. Nadeau from the Upper Cretaceous *Exogyra costata* zone.

Specimen 113.	Belemnite 8 mm. diameter	16·1°C.
114.	Belemnite 8 mm. diameter	15·5°
115.	Belemnite 10 mm. diameter	16·7°

These results may be compared with those of Urey et al. 1951, p. 412, whose value was 15·7°C., which may be low by 1 to 2°C. (p. 416). Lowenstam and Epstein (1954, p. 221) got 17·5°C. for four Cream Ridge belemnites.

A series of isotope palaeotemperatures taken at intervals through a rostrum from Wood Duck Creek (Fig. 7A) gave a simple curve. However, a specimen from Primrose Springs gave a double curve, as also did one from Lake Eyre (Fig. 7C). Urey et al. (1951), for a specimen of approximately the same size as that giving the curve Fig. 7C, obtained four highs and four lows in their curve (interpreted as four summers and four winters) whereas the writers obtained three summers and two winters. No significance is attached to this difference, nor do we think that our wider sections have obscured any seasons.

Lowenstam and Epstein (1954, p. 224) give an isotope analysis of a belemnite from the Tambo Series (Upper Albian) of the Hughenden District, Queensland. The isotope temperature is within the range of those obtained by us.

Permian Fossils

Professor K. E. Caster and one of us (E.D.G.) suggested that the great abundance of calcic matter in certain Permian beds in Tasmania, and the presence of large numbers of large, thick, calcareous shells, might well mean that the sediments were laid down in warmer interglacial times and not during glaciations as locally proposed. It was difficult to find calcareous material in the glacial beds, but a specimen was obtained from the Woodbridge glacial formation, 5 ft. below the Risdon Sandstone at Granton, Tasmania. Banks and Hale (1957) have described the stratigraphy. The other specimens are from the Berriedale Limestone and Peters Limestone which are believed to be of the same age. The samples were procured through the kind co-operation of Professor S. Warren Carey and Mr. M. R. Banks of the University of Tasmania. The specimens were somewhat suspect because of evidence of recrystallization, but the assays were made in the hope that they might throw light on the ecology of the formations concerned. The Woodbridge sample gave an $0^{18}/0^{16}$ temperature of $\sim 50°C$. which is obviously wrong; it is inferred that ionic exchange has occurred. The other assays yielded the following results:

Specimen 116.	Mollusc from Berriedale Limestone (for Tasmanian limestones see Hughes 1957) in quarry near Granton, Tasmania	21·5°C.
117.	Another mollusc from the same locality ..	22·5°
118.	Mollusc from Peters Limestone, Friendly Beaches (hill above end of track), near Coles Bay, E. Tasmania	19·4°

Since the palaeotemperature obtained from the Woodbridge glacial formation is obviously incorrect, the original intention to contrast its temperature with those of the calcareous formations cannot be carried out. Nevertheless, the following observations may be made:

1. The temperatures from the assays of molluscs from the Berriedale and Peters limestones are of tropical to subtropical level.

2. Although Banks and Hale (1957, p. 54) found that much of the ground-mass in the Berriedale Limestone (e.g.) is recrystallized, yet the temperatures are internally consistent.

3. Brill (1956) and Banks and Hale (1957) record erratics up to a foot in length in the limestone, some of which are facetted, and one of which was striated. One interpretation (preferred by the writers quoted) is that these are drop pebbles from ice masses, while another possibility is that they are rafted pebbles transported in tree roots and by such means (Emery 1955).

The oxygen isotope analyses have contributed some new and independent evidence, but has not solved the problem as to whether the calcareous formations are glacial or interglacial.

Experimental Procedure

The mass spectrometer differed from those employed by previous workers in this field in that it was a 180° type instrument. It was found to have excellent stability and the overall accuracy obtained appeared to be at least of the same order as that claimed by the American workers (i.e. $\pm 0{\cdot}5°C$.).

A. Mass Spectrometer and Electronic Circuits

The mass spectrometer was a 5 in. radius, single focussing instrument made by Consolidated Engineering Corporation (Model 21·103). It was modified by the addition of a double collector of the type described by Nier (1947). This was constructed from stainless steel plates insulated with glass balls. The plates were cleaned before assembly by electro-polishing. The ion beams at masses 44 and 45 were collected on one plate of exposed width 6·5 mm. whilst the beam at mass 46 passed through a 1·3 mm. slit to a cup.

Optimum values were employed for the potentials applied to the repeller and ion source focussing electrodes. An ionizing electron energy of 50 volts was used with a trap current of 5μA. The existing trap current regulator was inadequate so it was replaced by an improved circuit giving a regulation of better than 1 part in 2000. It was found that a change of 0·06μA in the trap current altered the output of the balancing circuits by $\sim$0·2 per mil (corresponding to 0·8°C.). The ion source temperature was maintained at 250 ± 0·1°C.

The magnet current was always adjusted so that the ion peaks came to focus with an ion accelerating voltage of 1KV ± 5 volts, this voltage being obtained from dry batteries.

One drawback to the arrangement used was the long lead ($\sim$ 10 in.) used to connect the collectors to their associated pre-amplifiers which were mounted outside the magnetic field. In spite of shielding, serious pick-up of random noise occurred. In the output of the balance recorder this noise was usually of the order of 0·2 mV peak to peak. The most favourable value obtained was 0·1 mV.

The output resistors for the 44 plus 45, and the 46 peak, amplifiers were 10^{10} and 10^{12} ohm respectively (Morganite Crucible Company). Mullard type ME1402 tubes were used for the pre-amplifier stages and were followed by conventional D.C. amplifiers of type described by Valley and Wallman (1948), 100% overall negative feedback being used. The output from the 44 plus 45 amplifier was passed through a decade potentiometer box and part of it balanced against the 46 amplifier output. It was found necessary to isolate the outputs of the two amplifiers from the Brown recorder used to record the balance, by means of two cathode follower triodes otherwise undesirable feedback effects occurred. The times of response of the two amplifiers were adjusted to be equal so that satisfactory response of the balance recorder to transients was obtained. Considerable care was taken in the selection of all tubes for low noise and microphony. Battery supplies were used for all filaments and HT supplies except the 44 plus 45 amplifier.

The Fig. 7 trace shows two samples recorded alternately and having a difference of 3.0°C. In practice a longer time was usually allowed for each sample trace and at least six comparisons made to give a reading to ± 0·5°C.

The molecular leak of the mass spectrometer was replaced by steel viscous flow leaks and a magnetic glass valve switch [Wanless and Thode (1953), Halsted and Nier (1950)]. The steel tubing was 25 in. long, 0·024 in. outside diameter, 0·010 in. inside diameter and the part clamped was previously annealed at a dull red heat in hydrogen. Equality of the leaks was tested every few days using the 44 peak height of the standard gas. The magnetic valve switches leaked very slightly and a small correction of the order of 0·1°C. was applied to the results—this correction being determined using several very highly enriched CO_2 samples.

B. Preparation of Samples and CO_2

Urey et al. (1951) examined belemnites that had lost their translucent character and found that their isotopic composition was the same as surrounding chalk. Thus any exchange reactions between shell carbonate and water could be expected to destroy the temperature record of a fossil shell. They point out that the best structures for preserving the record would be hard non-porous calcitic crystals and they have given an approximate calculation showing that for a 1 mm. calcite crystal at 20°C., 96% of the original record should still be retained after 7 x 10^8 years con-

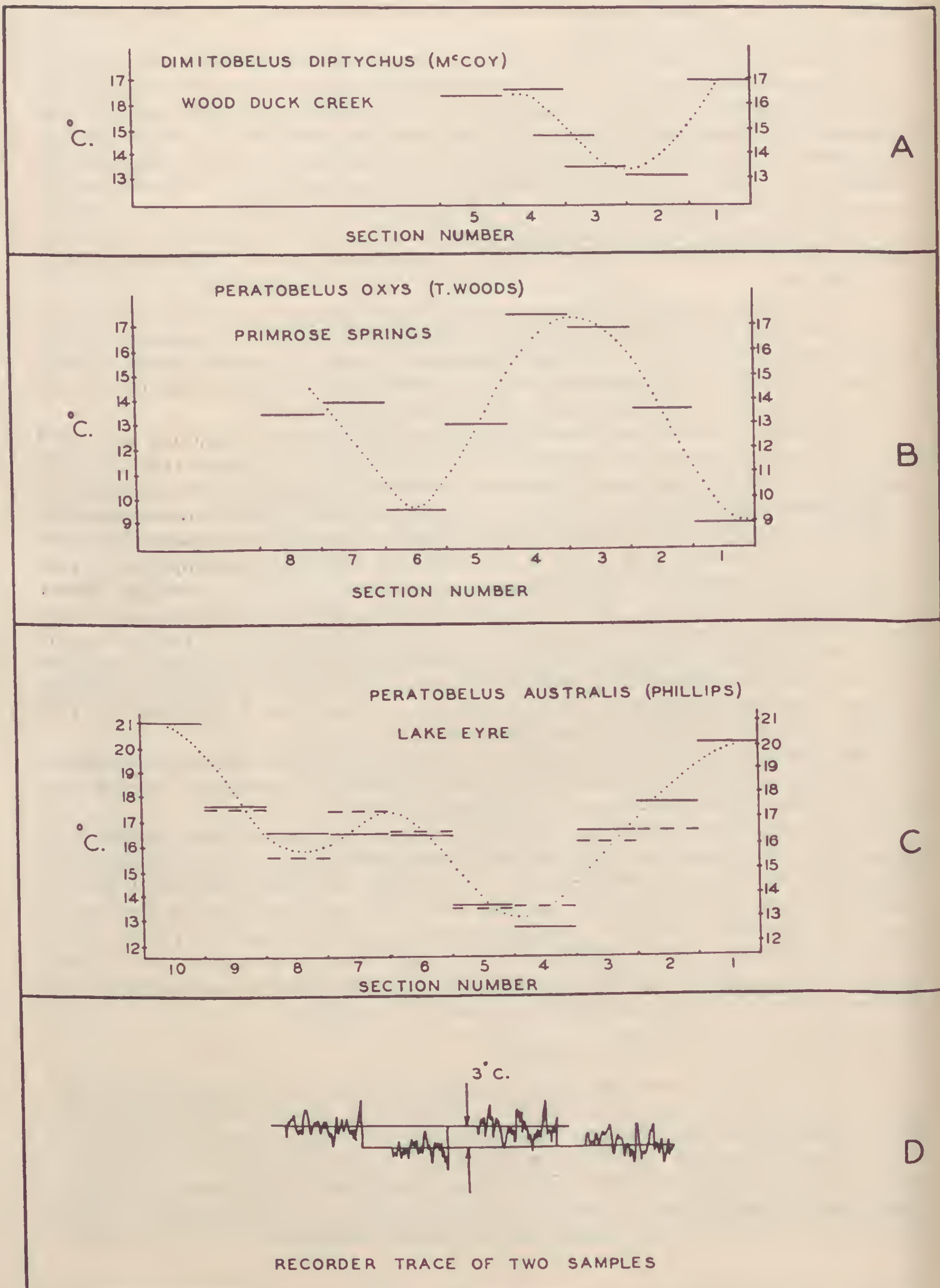

FIG. 7.—Sections through belemnites, and a typical recorder trace.

sidering a simple diffusion effect of Ca^{2+}. Percolation of water through a shell could of course alter the isotopic composition much more quickly than this.

Considerable care was exercised in the selection and preparation of shells used here. Only hard shell carbonate was used and wherever possible small, thin or porous shells avoided. The method of preparation was to smash the shell into several fragments and then to clean the surface of a large piece with a dental drill using steel burrs. A number of shells had obvious thin chalky surface layers and these were always completely removed. Smaller shells had their entire surfaces cleaned before being crushed. The grinding of the shells was done in an agate mortar and the powder stored in sample bottles in desiccators containing silica gel (cf. Craig 1957, p. 147). The temperature determinations were made, except for some duplicates, etc., within a few days of preparing the powder [cf. Epstein et al. (1953), p. 1321]. The shell specimens selected were nearly all white or off-white to light grey and any that were more highly discoloured than this were not used.

Epstein, Urey and co-workers heated their carbonate powder to 470°C. for 30 minutes in a stream of helium before preparing the CO_2. They give tables and graphs showing a smaller scattering of results after this treatment than without it. We have not used this heat treatment here for our main results for two reasons:

1. Epstein et al. (1951) had some unfortunate trouble with oxygen impurity in their helium, during their first determinations, altering the O^{18}/O^{16} ratios by an average of 1.1°C. with a spread of —0·6° to +2·2°C. We preferred to avoid the risk of this and by carefully selecting only good hard shells to minimize this type of scattering. That we have succeeded would appear to be shown by the results of Table 2 where five shell powders were heated at 470°C. *in vacuo* for 30 minutes and no significant temperature changes found. What the heating does to the carbonate powder, apart from changing it from a white to a greyish colour, is not certain. Epstein and co-workers (1951, p. 423) consider that organically precipitated calcium carbonate is decomposed whilst the possibility that organic matter is decomposed is also possible. Both of these are feasible but should be minimized for our samples.

2. The second reason for not running more heat treated samples was that the probable scattering due to impurity should be rather less than the "salinity" uncertainties.

TABLE 2

Heat Treatment (470 ± 5°C., in vacuo for 30 min.)

Spec. No.	Original Sample	After Treatment °C.	Before Treatment °C.	Remarks
16	*Anadara trapezia*	8·4	8·4	No change
10	*Nacella delesserti*	2·8	2·6	No change
101	*Notostrea tarda*	12·9	12·7	Duplicate 13·1°C. No change
75	*Chlamys antiaustralis*	16·2	16·7	No change
65	*Ostrea manubriata*	12·5	13·2	Slight lowering
11	Green algae from surface	12·5	11·0	Black powder after heating obviously from organic material

The CO_2 gas was prepared using 100% phosphoric acid (S.G. 1·87) prepared by adding P_2O_5 to 85% acid. Several drops of chromium trioxide were added to give a permanent light red colour which was reduced to a clear green with hydrogen peroxide the excess of which was decomposed by heat. About 0·1 gm. of carbonate powder was placed in the side arm of a T-shaped tube and 5 ml. of acid in the bottom. After evacuation and degassing of the acid by gentle heating the T tube was immersed in a 25·0 ±0·1°C. water bath and the powder tipped into the acid. After 30 minutes the CO_2 was collected in a liquid air trap to a residual pressure of about 10^{-2} mm. (probably air and water vapour). Dry ice and liquid air traps were next used to remove the air and water vapour impurities. Initially the glass handling apparatus was cleaned with soapy water only and then well flushed with standard gas. Memory effects were checked by repeat analyses and shown to be negligible over our range of isotope variations.

C. General Operation

The pressures of the sample and standard CO_2 were adjusted to equality using a Foord spoon gauge which could be read to 0·06 mm. Hg. The gas volumes were 250 c.cm. ($\sim$ 5 cm. Hg. pressure) and in one hour the CO_2 escaping through a viscous leak gave a pressure drop of 0.13 mm. Hg. A check on the effect of differing sample and standard pressures was made and found to be equivalent to 0·2 per mil for 1 mm. Hg. pressure difference. This change in the record trace occurred immediately and this order of time is in rough agreement with Kistemaker's Table 2 line 4 where our $R = 0{\cdot}012$ cm., $L = 64$ cm., $r \sim 10^{-3}$ cm., $1 = 0{\cdot}01$ cm. (estimated).

The time for a run was usually about 30 minutes, starting 10 minutes after flowing the gases through the leaks. A check was made to try and detect any fractionation change by flowing a portion of standard gas through one leak for 14 hours and then testing against the standard. No change was found.

The cold traps on the mass spectrometer were used without modification and consisted of a large liquid oxygen trap followed by a dry ice trap next to the mercury diffusion pumps and a dry ice trap between the diffusion pumps and the rotary oil pump. No special precautions were found to be necessary but the liquid oxygen level was raised intermittently during the day and degassed after several runs. Pumping was continuous over week-ends when cold air at —10°C. was blown into the dry ice trap.

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Description of Plate VIII

Figs. 1-2.—Typical belemnite. Two views of holotype rostrum of *Dimitobelus diptychus* (McCoy).
Fig. 3.—Transverse section of rostrum of *Peratobelus australis* (Phillips) showing sections assayed. See Fig. 7C for palaeotemperatures. Dark parts *a* and *b* discarded.
Fig. 4.—Transverse section of rostrum of *Dimitobelus diptychus* (McCoy) showing sections assayed. See Fig. 7A for palaeotemperatures.
Fig. 5.—Transverse section of *Peratobelus oxys* (Tenison-Woods) showing sections assayed. See Fig. 7B for palaeotemperatures. Black parts discarded.

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